



Department of Pesticide Regulation



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MEMORANDUM

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SUBJECT: PRELIMINARY RESULTS OF PESTICIDE ANALYSIS AND ACUTE TOXICITY TESTING OF MONTHLY SURFACE WATER MONITORING FOR THE RED IMPORTED FIRE ANT PROJECT IN ORANGE COUNTY, NOVEMBER 2000 (STUDY 183)

SUMMARY

During November 2000, surface water samples were collected from ten sites in Orange County, California. Water samples showed no detects of fenoxycarb, hydramethylnon, pyriproxyfen, dimethoate, and methidathion. Bifenthrin was detected at 0.122 and 0.307 parts per billion (ppb) from two commercial nursery sites. Toxicity was tested at San Diego Creek at Campus Drive, an integrated site. This site was significantly toxic (100% mortality) to *Ceriodaphnia dubia* in the water collected. Toxicity may be attributed to chlorpyrifos that was above the LC₅₀ for *C. dubia*. At a nursery site a filter strip and settling pond has been added to the drainage to mitigate offsite movement of insecticides and nitrates. At the time of this sampling, *Canna* had been planted throughout the filter strip. There was a general trend of declining concentrations of bifenthrin and chlorpyrifos as the water passed through the filter strip.

SCOPE OF THIS MEMORANDUM

This memorandum reports results of water sampling conducted by the Department of Pesticide Regulation (DPR), under interagency agreement with the California Department of Food and Agriculture (CDFA), for the Red Imported Fire Ant (RIFA) control project. Data included here are from the November 15 and 16, 2000 monitoring, and encompass results from both chemical analyses and aquatic biotoxicity testing. This memorandum summarizes results for bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, and five organophosphorus insecticides: chlorpyrifos, diazinon, dimethoate, malathion, and methidathion. Only bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, and chlorpyrifos are used in the RIFA control program. The other four organophosphates are in our multiresidue analytical method and are included in this report to assist in the interpretation of the toxicity results. Acute toxicity results using



Ceriodaphnia dubia are also included. An in-depth interpretation of data is not included here, but will be provided in the final report when the 2000 pesticide use report becomes available.

Reports of the monthly surface water sampling events will continue through the conclusion of the study. This memo is the fifteenth in the monthly sampling series. You can request previous sampling results memos by calling the number above or you may view or download them from DPR's website at <www.cdpr.ca.gov/docs/rifa>.

MATERIALS and METHODS

Sample and Data Collection

On November 15 and 16, 2000, surface water samples were collected at ten sites within the Orange County treatment area (Table 1 and Figure 1) including one rinse blank. Site G was sampled at the outflow of the vegetative filter strip (see mitigation sampling). Toxicity sample was collected at site E. This sampling event did not coincide with measurable rainfall.

Table 1. Sampling site descriptions in Orange County, California

Site #	Description	Coordinates
A	Bolsa Chica Channel at Westminster Ave.	N 33°45'35", W 118°02'36"
B	East Garden Grove Channel at Gothard St.	N 33°43'03", W 117°59'59"
C	Westcliff Park	N 33°37'24", W 117°54'02"
D	Bonita Creek at San Diego Creek	N 33°39'03", W 117°51'49"
E	San Diego Creek at Campus Dr.	N 33°39'18", W 117°50'44"
F	Hines at Weir	N 33°42'30", W 117°44'19"
G	El Modeno Gardens	N 33°42'43", W 117°44'16"
H	Marshburn Slough at Irvine Blvd.	N 33°41'45", W 117°44'02"
I	San Juan Creek at Stonehill Dr.	N 33°28'31", W 117°40'43"
J	Arroyo Trabuco at Oso Parkway	N 33°35'06", W 117°38'09"

All water samples were collected at center channel using a 10-liter stainless steel bucket and divided into one-liter amber sample bottles using a Geotech® 10-port splitter. Samples designated for organophosphate chemical analysis were preserved by acidification with 3N hydrochloric acid to a pH between 3.0 and 3.5. Because diazinon rapidly degrades under acidic conditions, it was analyzed from a separate, un-acidified sample. Samples designated for toxicity testing were delivered to the testing laboratory within 36 hours of collection. All samples were stored on wet ice or in a 4° C refrigerator until transported to the appropriate laboratory for analysis.

Mitigation Sampling

In addition to the monthly surface water samples being collected at sites throughout Orange County, mitigation samples are being collected at El Modeno Gardens (site G). A concrete lined ditch approximately 160 yards long, three and a half feet deep, and four to six feet wide. The filter strip consists of six successive settling basins planted with *Canna x 'Tropicana'* with additional unplanted basins at either end. Water samples are collected at the inlet and outlet of the filter strip. Rodamine dye was added to water at the inflow of the filter strip immediately after sampling. The purpose of the dye is to ensure that the same surge of water is sampled at the inflow and the outflow of the filter strip. Water at the outflow is then sampled just prior to the dye exiting the filter strip. During the November 16 sampling, water samples were taken twice approximately four hours apart. At the time of this sampling *Canna* had been planted throughout the filter strip. No sediment samples were collected during this sampling. A settling pond has also been installed before the water enters the filter strip. No samples were collected from the settling pond during this sampling.

Water samples are collected and transported using the technique described previously. Sediment samples are collected by submerging a 500-mL polycarbonate container and scooping up the sediment and stored on dry ice until delivery to the laboratory for analysis.

Toxicity Tests

Acute toxicity testing was conducted by the Department of Fish and Game (DFG) Aquatic Toxicity Laboratory following current U.S. Environmental Protection Agency (U.S. EPA) procedures using a cladoceran, *Ceriodaphnia dubia*, (U.S. EPA, 1993). Acute toxicity was determined using a 96-hour, static-renewal bioassay in undiluted sample water. Data were reported as percent mortality.

Environmental Measurements

Water quality parameters measured *in situ* included temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO). Water pH was measured using an IQ Scientific Instruments® (model IQ 150) pH meter. EC, water temperature, and DO were measured using an YSI® multi parameter meter (model 85). Additionally, the DFG Aquatic Toxicity Laboratory measured alkalinity, hardness, and ammonia on the samples to be tested for toxicity. Totals of alkalinity and hardness were measured with a Hach7 titration kit. Ammonia was determined using an Orion® 95-12 ammonia selective electrode attached to an Orion® specific ion meter (model 290A).

Insecticide Analyses

All water samples were analyzed for bifenthrin, fenoxycarb, hydramethylnon, pyriproxyfen, chlorpyrifos, diazinon, dimethoate, malathion, and methidathion. The CDFA Center for Analytical Chemistry performed all analyses using gas chromatography and a flame photometric detector for the five organophosphorus insecticides; a high performance liquid chromatography and a ultra violet detector for fenoxycarb, hydramethylnon, and pyriproxyfen; and gas chromatography with an electron capture detector confirmed with a mass selective detector for bifenthrin. The reporting limit (reliable detection levels) for chlorpyrifos and diazinon is 0.04 ppb, 0.1 ppb for fenoxycarb and pyriproxyfen, 0.2 ppb for hydramethylnon, and 0.05 ppb for the other insecticides.

RESULTS and DISCUSSIONS

Insecticide Concentrations

A total of fourteen water samples were analyzed for the five organophosphorus insecticides, bifenthrin and the three RIFA insecticide baits. Monthly surface water samples (Table 2) had no detectable residues of fenoxycarb, hydramethylnon, pyriproxyfen, dimethoate, and methidathion. Bifenthrin was detected in two samples taken from commercial nurseries at 0.122 and 0.307 ppb. Diazinon was detected in six samples and ranged from 0.045 to 0.513 ppb. Chlorpyrifos was detected in five samples and ranged from 0.049 to 0.277 ppb. Malathion was detected in two samples at 0.064 and 0.214 ppb. Sites F, G, and H drain commercial nurseries. Site F had detections of bifenthrin, chlorpyrifos and diazinon; site G had detections of bifenthrin and chlorpyrifos; and site H had a detection of chlorpyrifos. Samples collected at integrated site E, in a creek downstream from sites F, G, and H, showed detections of chlorpyrifos and diazinon. Sites C and D, which mainly drain urban areas, both had detections of malathion; site C had an additional detection of chlorpyrifos while site D had an additional detection of diazinon. Sites A and B also drain mainly residential areas and both had detections of diazinon. Of the nine insecticides tested, only chlorpyrifos, bifenthrin, fenoxycarb, hydramethylnon, and pyriproxyfen were allowed use in nurseries for treatment of fire ants to comply with U.S. Department of Agriculture's quarantine requirements. All of the organophosphorus insecticides listed are registered for uses in commercial agriculture, nurseries, golf courses or parks for the control of other insect pests. Malathion, diazinon, and chlorpyrifos are widely available for homeowner use.

Four surface water samples (Table 3) were taken as part of a mitigation study at site G. Bifenthrin and chlorpyrifos were detected in all samples ranging from 0.307 to 0.973 ppb for bifenthrin and from 0.049 to 0.128 ppb for chlorpyrifos. No other chemicals were detected in these samples.

Table 2. Insecticide concentrations and acute toxicity in monthly surface water samples, November 2000, Orange County, California.

Site	Concentration in pbb										% Acute Mortality ¹
	bifenthrin	fenoxycarb	hydramethylon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	malathion	methidathion	<i>C. dubia</i>	
A	ND	ND	ND	ND	ND	0.513	ND	ND	ND	NS ³	
B	ND	ND	ND	ND	ND	0.115	ND	ND	ND	NS	
C	ND	ND	ND	ND	0.052	ND	ND	0.214	ND	NS	
D	ND	ND	ND	ND	ND	0.053	ND	0.064	ND	NS	
E	ND	ND	ND	ND	0.277	0.094	ND	ND	ND	100/0	
F	0.122	ND	ND	ND	0.063	0.045	ND	ND	ND	NS	
G	0.307	ND	ND	ND	0.049	ND	ND	ND	ND	NS	
H	ND	ND	ND	ND	0.08	ND	ND	ND	ND	NS	
I	ND	ND	ND	ND	ND	0.07	ND	ND	ND	NS	
J	ND	ND	ND	ND	ND	ND	ND	ND	ND	NS	
RB ⁴	ND	ND	ND	ND	ND	ND	ND	ND	ND	NS	

¹ Two numbers are reported for each toxicity test. The first number is the result from the sample; the second from the corresponding control.

² ND = none detected at the reporting limit for that chemical.

³ NS = not sampled

⁴ RB = field rinse blank

Table 3. Insecticide concentrations in mitigation samples, November 2000, Orange County, California.

Location	Concentration in ppb								
	bifenthrin	fenoxycarb	hydramethylnon	pyriproxyfen	chlorpyrifos	diazinon	dimethoate	malathion	methidathion
<u>Surface Water Samples</u>									
Filter strip inflow I ¹	0.479	ND	ND	ND	0.08	ND	ND	ND	ND
Filter strip inflow II	0.973	ND	ND	ND	0.128	ND	ND	ND	ND
Filter strip outflow I	0.307	ND	ND	ND	0.049	ND	ND	ND	ND
Filter strip outflow II	0.513	ND	ND	ND	0.061	ND	ND	ND	ND

¹ Two sets of filter strip samples were taken; first set of data is from first sampling.

² ND = none detected at the reporting limit for that chemical.

Toxicity Data

Toxicity samples were taken from one integrated site within the treatment area. Sample from site E was acutely toxic to *C. dubia* causing 100 % mortality (Table 2). Site E drains an integrated site and had a detection of chlorpyrifos above the LC₅₀ for *C. dubia* (Table 4). All detections of bifenthrin were above the LC₅₀ for *C. dubia*.

Table 4. LC₅₀'s of insecticides (ppb) for three aquatic species.¹

Pesticide	Rainbow trout	<i>D. magna</i>	<i>C. dubia</i>
Bifenthrin	0.15	1.6	0.078 ²
Chlorpyrifos	10	0.1	0.13 ³
Diazinon	3200	0.96	0.51 ⁴
Dimethoate	8500	2500	NA
Fenoxycarb	1600	400	NA
Hydramethylnon	160	1140	NA
Malathion	68	1.0	1.14 ⁵ - 2.12 ⁶
Methidathion	10.5	7.2	2.2
Pyriproxyfen	>325	400	NA

¹ Data from CDPR, 2000.

² Data from CDFG, 2000.

³ Data from Menconi and Paul, 1994

⁴ Data from Menconi and Cox, 1994

⁵ Data from Nelson and Roline, 1998

⁶ Data from Ankley et al., 1991

Environmental Measurements

Table 5 presents the data for DO, temperature, pH, and EC. Ammonia, alkalinity, and hardness are only reported for site E since these measurements are taken with the toxicity tests. Water temperature ranged from 7.8 to 19.2° C; pH ranged between 7.8 to 9.5; DO ranged from 9.07 to 14.29 mg/L; EC ranged from 690 to 3237 µS/cm; ammonia was <0.1 mg/L NH₃; alkalinity was 246 mg/L CaCO₃; and hardness was 754 mg/L CaCO₃. The California Regional Water Quality Control Board, Water Quality Control Plan, Santa Ana River Basin (1995), and the Water Quality Control Plan, San Diego Basin (1994), list the following water quality guidelines as acceptable: water temperature no higher than 78°F (25.5°C), pH between 6.5 and 8.5, and DO above 5.0 mg/L. The Santa Ana River Basin plan determines ammonia levels to be dependent upon water temperature and pH, while the San Diego Basin plan states that ammonia levels shall not exceed 0.025 mg/L. The plans do not provide an acceptable range for EC, alkalinity, or hardness. The pH at sites C, F, and filter inflow II were above the maximum guideline.

Table 5. Water quality measurements at sampling sites, November 2000, Orange County, California.

Site	Temperature (°C)	pH	Dissolved Oxygen (mg/L)	Electroconductivity (µS/cm)	Ammonia (mg/L)	Alkalinity (mg/L CaCO ₃)	Hardness (mg/L CaCO ₃)
A	15.7	8.4	13.7	2333	NR	NR	NR
B	13.5	8.3	12.6	1180	NR	NR	NR
C	18.9	9.5	14.29	817	NR	NR	NR
D	8.5	8.2	10.64	3237	NR	NR	NR
E	13.9	8.4	11.23	2924	<0.1	246	754
F	16.1	8.7	9.85	2217	NR	NR	NR
G	10.6	8.5	13.71	1273	NR	NR	NR
H	15.5	8.3	9.56	690	NR	NR	NR
I	19.2	8.5	12.37	2367	NR	NR	NR
J	16.0	7.8	9.07	964	NR	NR	NR
Filter strip inflow I	7.8	8.4	12.15	1367	NR	NR	NR
Filter strip inflow II	18.2	8.8	10.74	862	NR	NR	NR
Filter strip outflow I	10.6	8.5	13.71	1273	NR	NR	NR
Filter strip outflow II	15.9	NT	11.99	1328	NR	NR	NR

NT= Not taken

NR= No reading available

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